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Water-Soluble Self-Doped Conducting Polyaniline Copolymer

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Polyaniline (PANI) has emerged as an important conducting polymer because of its good environmental stability, low cost, and high conductivity upon doping with acid.[1,2] The methods proposed to synthesize water-soluble conducting polyaniline involved either the attachment of water-soluble functional groups to its benzene rings or the replacement of in the N−H groups of PANI by water-soluble functional groups. Yue and Epstein[3,4] have synthesized sulfonic acid ring-substituted PANI (SPAN) by reacting the emeraldine base with fuming acid and obtained a conductivity of 0.1−1 S/cm. However, the polymer obtained became water-soluble only after its conversion to the salt form after undoping with a basic aqueous solution. The replacement of the sulfonic acid group with phosphoric acid yielded another water-soluble self-doped ring-substituted PANI, which exhibited, however, the low conductivity of 10^{-3} S/cm.[5] Hany et al.[6] attempted to synthesize a self-doped PANI by reacting the emeraldine base with propane sultone or butane sultone. However, the product had both a very low solubility and low conductivity ($\sim 10^{-9}$ S/cm). Through a variant of the latter method, an N-substituted water-soluble self-doped PANI, poly(aniline-*co*-propanesulfonic acid aniline) [PAPSAH], was synthesized by reacting the emeraldine base first with NaH and subsequently with propane sultone. PAPSAH could be cast into free-standing films directly from its aqueous solution and provided a conductivity of about 10^{-2} S/cm without external doping.[7] Another approach for the preparation of N-substituted water-soluble self-doped conductive PANI was the copolymerization of aniline with a suitable substituted aniline to generate copolymers. The copolymer thus obtained exhibited improved solubility in an aqueous NH_4OH solution;[8] however, its conductivity was low (10^{-3} S/cm). In conclusion, the above approaches synthesized water-soluble self-doped polyanilines by modifying the structure of the emeraldine base.

A new water-soluble self-doped copolymer, namely, poly(aniline-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid, [PAMPANI]), and its salt have been synthesized by us. Both PAMPANI and its salt could be dissolved in water and cast into films from their aqueous solutions.

The synthesis of PAMPANI is described in Scheme 1. *N*-(4-Anilinophenyl)methacrylamide (APMA) could be synthesized via the catalytic aminolysis reaction. The preparation procedure can be described as follows: 18.4 g (0.1 mol) of *p*-aminodiphenylamine, 40 g (0.4 mol) of methyl methacrylate, 1.24 g (0.05 mol) of dibutyltin oxide (as catalyst), and 0.02 g (0.0001 mol) of phenothiazine (as retardant of polymerization) were introduced into a 100 mL round-bottom three-neck flask fitted with a magnetic stirrer, a 40 cm vacuum jacketed Vigreux column, and a distillation head with a water-cooled condenser. The mixture was heated at low reflux and the methanol/methyl acrylate codistillation product removed continuously for over 11 h. The Vigreux column was then removed and replaced with a distillation head, and the remaining methyl methacrylate was distilled, while concurrently adding 25 mL of xylene. With stirring, an additional 25 mL of xylene was added at 130 °C and the mixture cooled to room temperature. The product was separated by filtration, washed with xylene, dried, and purified by recrystallization from ethanol. The AMPA obtained exhibited the following characteristics; mp 107 ± 1 °C. ^{1}H NMR ($CDCl_3$, δ ppm relative to Me_4Si): 2.0 (s,3H), 5.4 (s,1H), 5.8 (s, 1H), 5.9 (s,1H), 6.9−7.4 (m,9H), 7.5 (s,1H). MS (*m*/*e*): 252.2 (M^+), 183.2, 69. FTIR (cm^{-1}): 3353 (N−H), 3100−3059 (═CH), 1663 (C═O in amide), 1608 (C−NH def).

Poly(AMP-*co*-APMA) (AMP = 2-acrylamido-2-methyl-1-propanesulfonic acid) was prepared through a surfactant-free emulsion polymerization in water. A $4^1/_2$ g sample of AMP and 0.05 g of ammonium persulfate were dissolved in 40 g of distilled water present in a three-neck flask located in a water bath at 70 °C under a nitrogen atmosphere, and the mixture was stirred for about 1 h. Then, 0.5 g of AMPA in 10 g of chloroform was slowly added dropwise and the reaction allowed to last for 4.5 h. This was followed by filtration, and the water of the filtrate was removed by evaporation to obtain a pale yellow poly(AMP-*co*-AMPA). FTIR (cm^{-1}): 3345−3245 (N−H); 1662 (CO−NH−alkyl); 1640 (CO−NH−aromatic); 1190 and 1054 (O═S═O, asymmetric and symmetric stretchings). ^{1}H NMR (D_2O, ppm): 1.3 (s, CH_3), 1.8−2.0 (m, CH_2), 3.0−3.4 (m, CH_2-SO_3 and CH−CO), and 7.0−7.4 (m, aromatic hydrogen). AIBN could not be used as initiator because a large amount of an insoluble precipitate (poly(AMPA)) was generated.

The graft copolymerization of aniline onto poly(AMP-*co*-AMPA) was carried out by the dropwise addition of 20 g of 2 wt % poly(AMP-*co*-AMPA) and 10 g of 8 wt % APS aqueous solutions to an aniline (0.8 g)/1 M HCl aqueous solution of pH < 2. After 4−6 h of reaction, the product was precipitated from a dark-green solution with a 1 M HCl aqueous solution, and after filtration the green precipitate was washed several times with deionized water and then undoped with a 1 M NH_4OH aqueous solution to yield a blue-violet solution. The polymer, PAMPANI−NH_4, was further purified and converted into PAMPANI by the ion exchange of NH_4^+ with H^+, using a H^+-type ion-exchange resin (IR 1200H resin from Aldrich), to yield a pure green PAMPANI aqueous solution. The PAMPANI solution was concentrated in a vacuum evaporator, and a film was obtained by casting from solution.

The conductivity was first measured after the specimen was allowed to dry for 24 h in air and later during its drying for 48 h in the high vacuum of 30 mbar at 40 °C. The conductivity was measured by the four points method in a drybox under N_2. The experimental results are plotted in Figure 1, which shows that the conductivity became constant after about 12 h of drying in high vacuum.

The FTIR spectrum of PAMPANI−Na (obtained by neutralizing the PAMPANI solution with a NaOH

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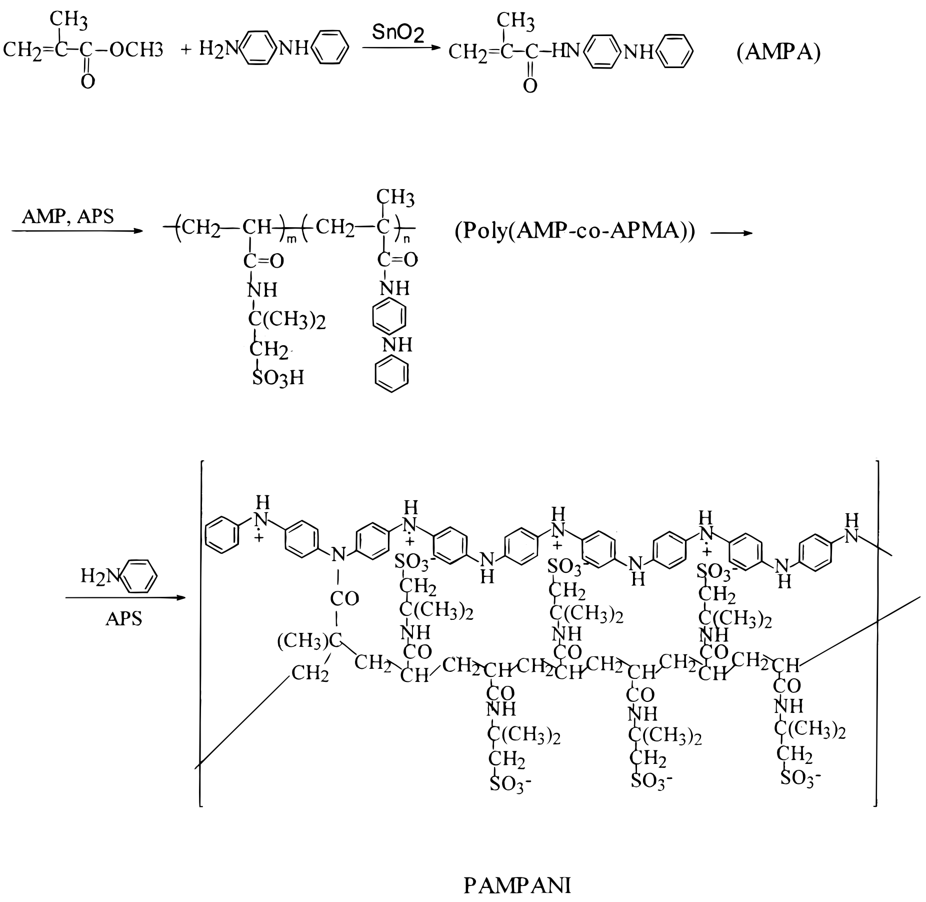
Scheme 1



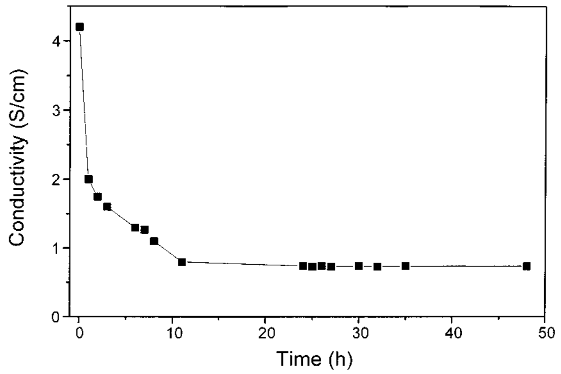


Figure 1. Conductivity vs the drying (in a vacuum) time of a thin film (thickness: 1 μm).

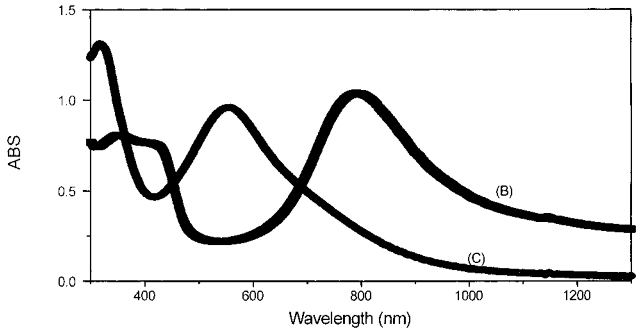


Figure 2. UV/vis spectra of PAMPANI: (B) aqueous solution, (C) aqueous solution after neutralization with 1 M NH_4OH.

aqueous solution (pH = 12)) exhibits peaks at 1171 and 1057 cm^{-1}, which can be assigned to the asymmetric and symmetric O=S=O stretching vibrations, respectively, indicating the existence of SO_3^- groups.[9] The peaks at 1592, 1506, and 1313 cm^{-1} are due to the quinoid ring, benzeneoid ring, and $C_{aromatic}$−N stretching vibration, respectively, of the emeraldine segment of the PAMPANI−Na. The absorption peak at 1651 cm^{-1}, which can be assigned to the −CO−N⟨ (tertiary amide) stretching vibration, indicates that PAMPANI is a copolymer of PANI and poly(AMP-*co*-AMPA). Compared to those of PAMPANI−Na, the peaks corresponding to the quinoid and benzeneoid rings of PAMPANI are shifted to lower frequencies by 29 and 32 cm^{-1}, while that due to the $C_{aromatic}$−N stretching vibration is shifted from 1313 to 1303 cm^{-1}. These shifts are similar to those observed when emeraldine was doped with sulfonic acid[10,11] and reveal that PAMPANI is in a self-doped state.

The ^1H NMR spectrum of PAMPANI (D_2O as solvent) exhibits multipeaks around 7.9, 8.5, and 8.7 ppm, which can be attributed to the hydrogens of the benzenic ring, a peak at 1.4 ppm, which can be assigned to the hydrogens of the methyl groups, broad peaks at about 2.0 ppm, which can be attributed to the hydrogens of $-CH_2-$, and peaks at about 3.2 ppm, which can be attributed to the hydrogens of $-CH_2-SO_3$ and −CH−CO.[12] These results are in agreement with the FTIR results and with the structure proposed for the PAMPANI conducting polymer (Scheme 1).

The fact that PAMPANI is in a self-doped state is also confirmed by the electronic spectrum of its aqueous solution (Figure 2), which exhibits a $\pi-\pi^*$ transition of the benzenoid rings[13] at 352 nm and polaron/bipolaron band transitions[14] at 477 and 791 nm. When the PAMPANI solution was converted to PAMPANI−NH_4

by neutralization with 1 M NH_4OH aqueous solution, the polaron/bipolaron band disappeared, and a strong exciton transition of the quinoid rings[15] appeared at 556 nm.

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